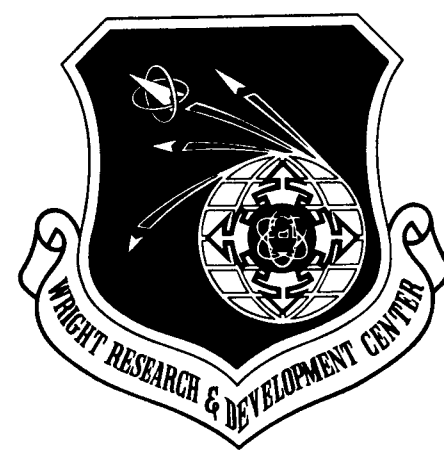


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GRAFT COPOLYMERS OF RIGID-ROD

POLY(P-PHENYLENEBENZOBISIMIDAZOLE)

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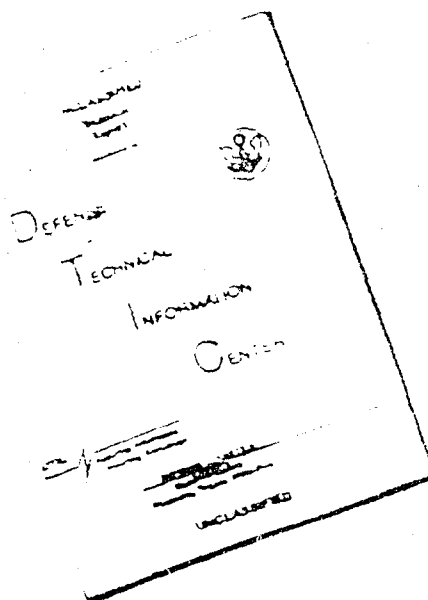
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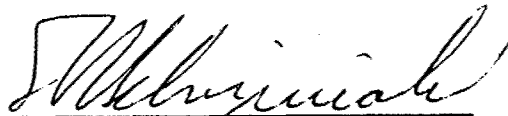
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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2303, "Nonmetallic and Composite Materials," Task No. 2303Q3, Work Unit Directive 23303Q307, "Structural Resins." It was administered under the direction of Materials Laboratory, Wright Research and Development Center, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr R. C. Evers as the Materials Laboratory Project Scientist. Coauthors were Dr R. C. Evers, Materials Laboratory (WRDC/MLBP), Mr T. D. Dang, Systran Corporation, and Mr D. R. Moore, Universal Energy Systems.

This report covers research conducted from June 1986 to June 1987. The authors thank Mr E. J. Soloski for the thermogravimetric analysis data and Dr E. G. Jones for the thermogravimetric-mass spectral analysis. Dr Satish Kumar performed the electron microscopy and x-ray experiments. Ms Lisa Denny provided advice for the polymer processing work.

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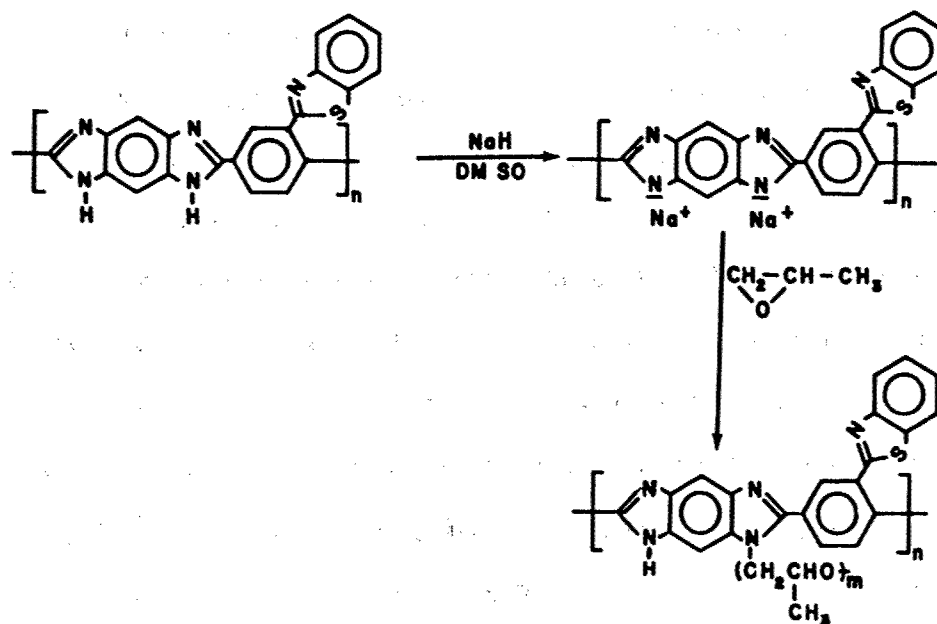
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SECTION I

INTRODUCTION

Rigid-rod aromatic-heterocyclic polymers such as poly(p-phenylenebenzobisthiazole)¹ and poly(p-phenylenebenzobis-oxazole)² can be prepared in high molecular weight in a polyphosphoric acid reaction medium and can be spun into high-strength and -modulus fibers and films.³ These thermo-oxidatively stable polymers are being considered for various Air Force severe environment applications requiring high specific strength and modulus. However, development for applications requiring bulk forms has been hindered by the difficult processibility of these polymers due to their limited solubility (strong acids only, e.g. methane-sulfonic acid, polyphosphoric acid) and complete infusibility. In order to improve the processibility of the rigid-rod polymers, a research effort is being carried out to increase solubility and/or fusibility through modification of the polymer backbone. Other researchers have demonstrated that substantial changes in polymer solubility and fusibility characteristics as well as mechanical properties can be achieved through grafting of flexible polymer chains onto relatively rigid polyaramide backbones.⁴⁻⁸ These reactions have been carried out by abstraction of an acidic proton from the amide group followed by reaction of appropriate vinyl⁴⁻⁷ or epoxy⁷⁻⁸ monomers with the resultant soluble anion. Under the

current effort, sodium methylsulfinylmethide in dimethyl sulfoxide (DMSO) is used to abstract the acidic protons from the benzobisimidazole groups of a rigid-rod polymer, poly(p-phenylenebenzobisimidazole) with a pendant 2-benzothiazole group (PPBI). This technique had been used by Marvel several decades earlier for solubilization and subsequent modification of polybenzimidazole structures.⁹ Following solubilization of PPBI, grafting of propylene oxide (PO) onto the benzimidazole anions in the polymer backbone leads to rigid-rod graft copolymers which contain flexible polypropylene oxide (PPO) side-chains and which are designated here as PPBI-g-PPO.



In this technical report, the synthesis of these graft copolymers is described as is their preliminary characterization and some initial processing work.

SECTION II

RESULTS AND DISCUSSION

1. GRAFT COPOLYMER SYNTHESIS

Initial efforts were directed toward selection of an appropriate rigid-rod polymer for the grafting studies. Poly(p-phenylenebenzobisimidazole)¹⁰ and its articulated analogs^{11,12} proved to be completely inert to the solubilization process. However, samples of PPBI provided by Tsai and Arnold¹³ dissolved readily upon contact with sodium methylsulfinylmethide in DMSO to form a deep red solution. Subsequently, larger quantities of PPBI were synthesized, albeit in lower molecular weight than reported by Tsai and Arnold,¹³ and subjected to solubilization and subsequent grafting reactions with PO. It was necessary to maintain metallation at or near 100 percent in order to achieve solubility of the PPBI in the DMSO medium. This requirement precluded control of the number of graft sites on the polymer backbone. After holding the metallated polymer under standard reaction condition (30-60C, 18-24 hours), no polymer degradation or scission could be observed upon regeneration of the parent polymer. Following isolation of PPBI-g-PPO at the conclusion of the grafting reaction, it was initially extracted with water to remove solvent and inorganic salts and then with acetone to separate any ungrafted PPO homopolymer that was generated during the grafting procedure.

The results of the grafting reactions are listed in Table 1. The PO conversion and the copolymer composition were calculated as follows:

$$\% \text{ Conversion of PO} = \frac{\text{Yield Wt} - \text{Starting Wt PPBI}}{\text{Starting Wt PO}}$$

$$\text{Wt \% PPBI} = \frac{\text{Starting Wt PPBI}}{\text{Yield Wt}}$$

Table 1. Synthesis of PPBI-g-PPO

Trial No	1 ^(a)	2 ^(a)	3 ^(a)	4 ^(a)	5 ^(b)	6 ^(c)	7 ^(c)
Monomer Feed- PO/PPBI (wt/wt)	88/12	80/12	67/33	54/46	80/20	80/20	88/12
(mole/mole)	50/1	25/1	12/1	7.5/1	25/1	25/1	50/1
Yield (%)	26	23	41	56	34	42	34
Conversion (%)	17	4	12	19	18	27	27
Copolymer Composition PPBI/PBO (wt/wt)	57/43	14/86	19/81	18/82	41/59	52/48	67/33
η_{inh} PPBI ^(d) (dl/g)	3.20	2.80	2.80	2.80	3.20	3.20	3.65
η_{inh} Copolymer ^(d)	2.85	2.65	2.01	2.03	2.88	2.78	1.35

- (a) Reaction run under a nitrogen sweep.
 (b) Reaction run in a sealed tube.
 (c) Reaction run under slight nitrogen pressure.
 (d) Methanesulfonic acid, 30°C, 0.20g/dl.

2. GRAFT COPOLYMER CHARACTERIZATION

The graft copolymers were obtained as fibrous, light-brown materials. The successful incorporation of PPO into the rigid-rod polymer structure was indicated by the infrared spectra of the copolymers (Figure 1). Strong absorptions were observed at $2900\text{--}2950\text{cm}^{-1}$ and 1100cm^{-1} , attributable to C-H and C-O stretching vibrations of PPO, respectively. The absorption at 3400cm^{-1} , attributable to the N-H stretching of the benzimidazole ring was somewhat diminished, indicative of successful grafting at that site in the PPBI chain. However, stretching vibrations of the terminal O-H groups in the grafted PPO chains would be expected to overlap this band and make quantitation of the grafting efficiency by infrared spectroscopy impossible. The solubility of PPBI was considerably modified by the grafting procedure. While PPBI was soluble only in polyphosphoric acid and methanesulfonic acid, the graft copolymers exhibited considerable solubility in methanesulfonic acid as well as other organic solvents such as 97% formic acid and trifluoroacetic acid. While the parent rigid-rod polymer readily exhibited stir opalescence in polyphosphoric acid and methanesulfonic acid, lyotropic solutions of PPBI-g-PPO in methanesulfonic acid could not be obtained.

Thermo-oxidative stability of PPBI was substantially lowered by the incorporation of PPO into the polymer structure. Because of the aliphatic nature of the grafted side-chains, onset of breakdown of PPBI-g-PPO under thermogravimetric analysis (TGA) in air

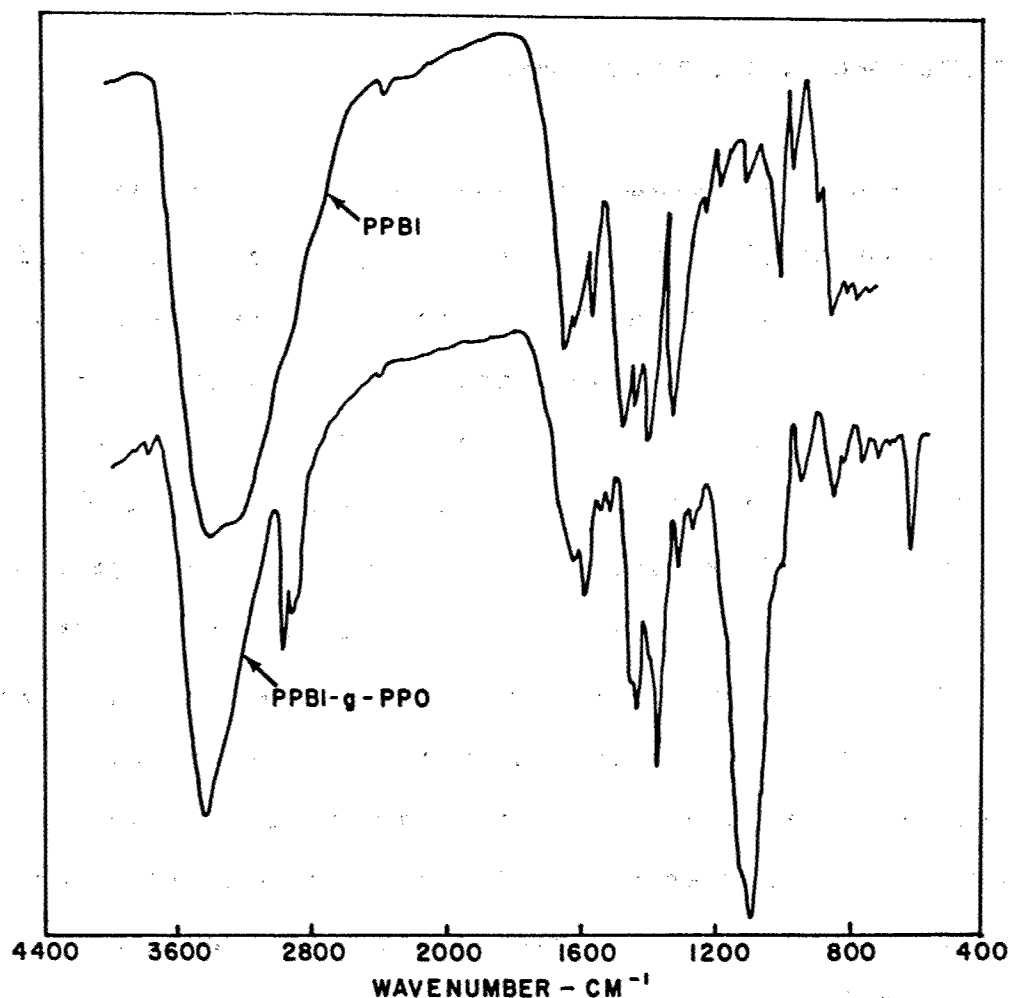


Figure 1. Infrared Spectra of PPBI and PPBI-g-PPO (KBr Pellet)

($\Delta T=10^{\circ}\text{C}/\text{min}$) occurred in the $250\text{--}275^{\circ}\text{C}$ range with almost complete weight loss having occurred by 650°C . Considerable variation in the thermo-oxidative stability of the graft copolymers was observed, dependent upon the amount of PPO side-chain in PPBI-g-PPO. In contrast, PPBI exhibited a small early weight loss due to absorbed water but did not undergo significant degradation until 525°C . Comparative TGA thermograms are shown in Figure 2. Thermogravi-

metric mass spectral analysis was performed in vacuo on PPBI-PPO. In the lower temperature regions, the major degradation products were PPO fragments, the majority of which were small species involving one or two PPO units (Figure 3). The next major product was benzothiazole arising from cleavage of the heterocyclic pendant group.¹³ At higher temperatures, substantial quantities of hydrogen cyanide and ammonia from main chain degradation were generated.

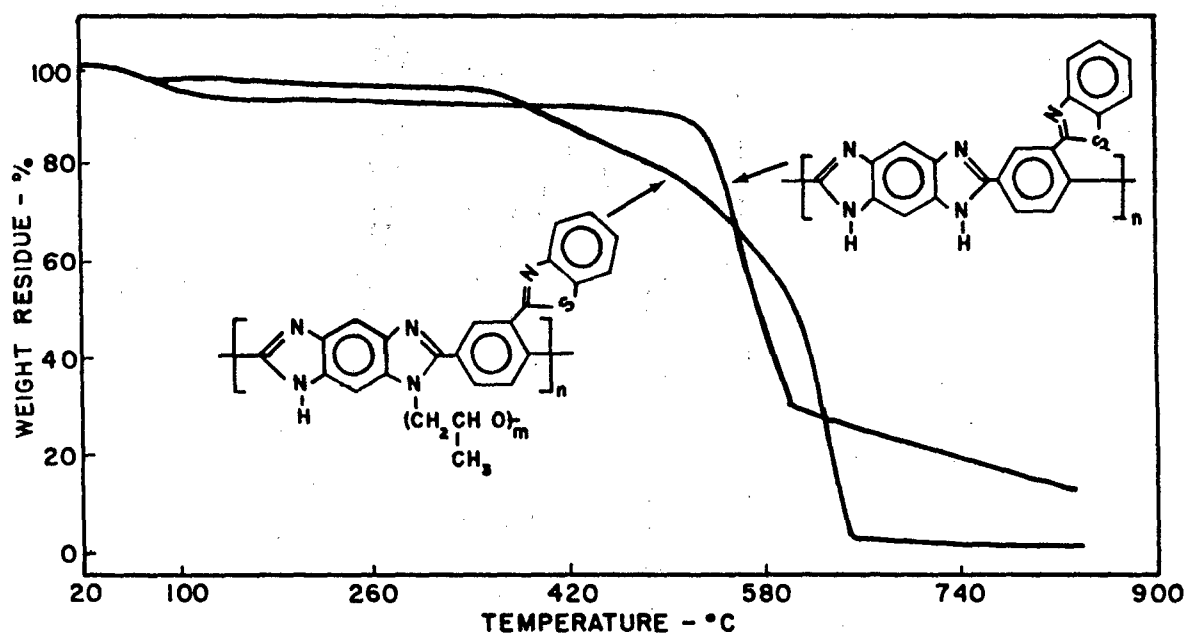


Figure 2. Comparative TGA Thermograms of PPBI and PPBI-g-PPO ($\Delta T=10^\circ\text{C}/\text{min}$).

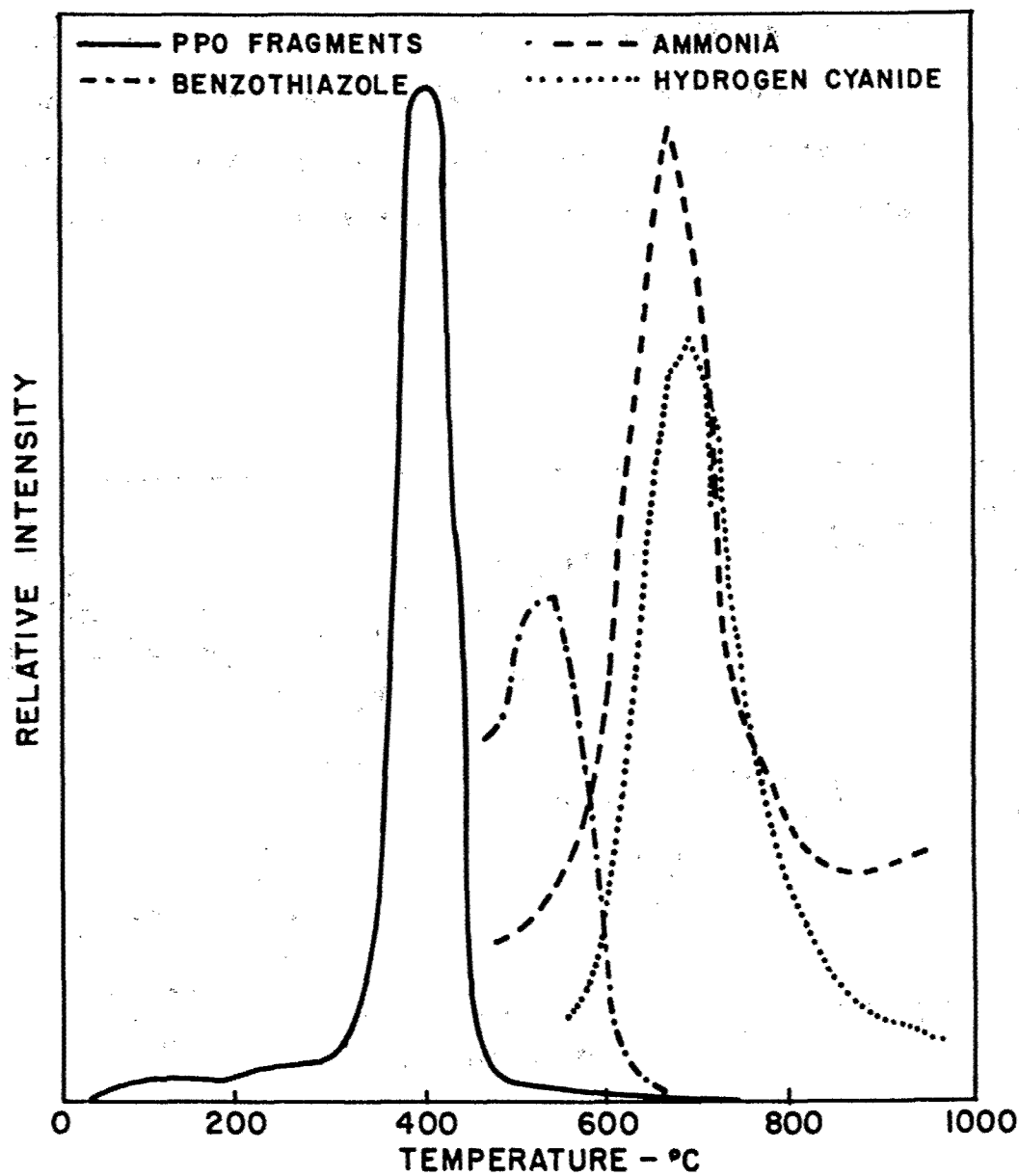


Figure 3. Thermogravimetric - Mass Spectral Analysis of PPBI-g-PPO ($\Delta T=3^{\circ}\text{C}/\text{min}$).

Although differential scanning calorimetry did not indicate softening behavior in PPBI-g-PPO, molded specimens could be fabricated from the graft copolymer through the application of elevated temperature and pressure. For example, a one-gram powder sample of PPBI-g-PPO (Trial 6) was heated for one hour in a steel mold at 375-450°F and 750psi to give a stiff, seemingly well-consolidated tensile bar. Based upon TGA data and physical observations during the consolidation process, the molding temperatures employed represented the thermo-oxidative stability limit of the PPO side-chains. Consolidation could not be effected at slightly lower temperatures (350-425°F) even though pressures up to 4000psi were employed. Cursory examination of the fracture surfaces of the fabricated specimens was carried out by wide angle x-ray scattering and electron microscopy. The x-ray diffraction patterns exhibited a sharp ring at 5.97Å which was also present in the parent polymer, PPBI, and a diffuse halo at 4.99Å, attributable to amorphous PPO. Electron microscopy indicated the presence of contaminant inorganic material and suggested that consolidation of the graft copolymer powder was incomplete.

SECTION III

CONCLUSIONS

While the current effort demonstrated that substantial changes in PPBI solubility and fusibility could be effected through grafting of PPO side-chains to the rigid-rod polymers, complete consolidation of the graft copolymers to molded specimens with acceptable tensile properties was not achieved. Consolidation was hindered by the modest thermo-oxidative stability of the aliphatic PPO structure which limited the upper temperature used during the molding process. Limitations in the polymerization processes excluded the synthesis of high molecular weight PPBI backbone and PPO side-chains necessary for good tensile properties of fabricated specimens. Synthesis efforts are currently underway to prepare well-defined, thermo-oxidatively stable rigid-rod graft copolymers of sufficient molecular weight to yield high strength and modulus along with ready processibility. These investigations will be reported in the future.

SECTION IV

EXPERIMENTAL

The parent rigid-rod polymer, PPBI, was synthesized by a literature procedure¹⁰ through the polycondensation of 1,2,4,5-tetraaminobenzene tetrahydrochloride with 2-(2-benzothiazyl)-terephthalic acid in polyphosphoric acid. A representative grafting reaction is described below.

A suspension of sodium hydride (0.66g) in freshly distilled DMSO (110g) was stirred under a nitrogen blanket at room temperature for 30 minutes followed by heating at 75°C for one hour. The resultant clear, light green solution was then cooled to 40°C and 3.00g of PPBT [η_{inh} = 3.20 dl/g (methanesulfonic acid, 30°C, 0.25 g/dl)] was added. Upon being stirred for 24 hours at this temperature, the resultant suspension gradually became homogenous and was converted into a deep red solution. This solution was heated at 60°C for 2 more hours to insure complete solubilization. It was then cooled to 30°C and 13.06g of PO along with 150g of distilled DMSO were added. Upon addition of PO to the metallated polymer solution, a substantial exotherm was observed. The reaction mixture simultaneously took on a dark brown color with an increase in viscosity. Gelatinous graft copolymer precipitated from solution over the course of several hours. After being allowed to stir at 30°C for 24 hours, the reaction mixture was added to dilute hydrochloric acid and the PPBI-g-PPO precipitate was isolated by

filtration. It was placed in 2000ml of dilute hydrochloric acid and broken into a fine suspension through vigorous stirring. The copolymer was extracted overnight in a Soxhlet extraction apparatus with water and then with acetone for 24 hours. The copolymer was dried under vacuum at 100°C for 24 hours. The yield was 6.80g, 41.6% theoretical yield (based on the weight of PPBI). An η_{inh} of 2.78dl/g (methanesulfonic acid, 30°C, 0.25g/dl) was recorded for PPBI-g-PPO.

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